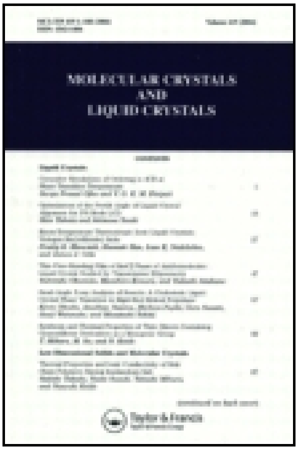

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Thermodynamic Approach to Electrochemical Lithium Intercalation into $Li_{1-\delta}Mn_2O_4$ Electrode Prepared by Sol-Gel Method

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Thermodynamic Approach to Electrochemical Lithium Intercalation into $Li_{1-\delta}Mn_2O_4$ Electrode Prepared by Sol-Gel Method

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Electrochemical lithium intercalation into $Li_{1-\delta}Mn_2O_4$ electrode prepared by sol-gel method was investigated from the thermodynamic view point by using galvanostatic intermittent titration technique (GITT) combined with EMF-temperature measurement. The electrode potential vs. lithium content curve was theoretically calculated with the aid of the lattice gas model based upon the Bragg-Williams approximation for the cubic spinel composed of two sub-lattices. Considering the considerable difference between both lithium contents in two sub-lattices due to the ordering of the intercalated lithium ions, the theoretical partial molar enthalpy and entropy were calculated at various lithium contents by a numerical method. From the comparison between the theoretical partial molar quantities and experimental results, the electrochemical lithium intercalation into the $Li_{1-\delta}Mn_2O_4$ electrode was discussed in terms of the ordering of the intercalated lithium ions.

Keywords: $Li_{1-\delta}Mn_2O_4$ electrode; order-disorder phase transition; partial molar enthalpy and entropy; lattice gas model; Bragg-Williams approximation

INTRODUCTION

In the last decade many researchers have devoted to the comprehensive thermodynamic study on the lithium intercalation to explain the most interesting phenomena such as order-disorder phase transition[1,2] and two-phase coexistence[2,3] in the lithium intercalation compounds. For this purpose such fundamental thermodynamic properties as the partial molar enthalpy and entropy for the electrochemical dissolution of lithium in the compounds have been experimentally determined from the temperature dependence of the electrode potential[4-6]. Several researchers have theoretically derived the relationship between the electrode potential and the lithium composition using simple statistical thermodynamics of the lattice occupancy in the compounds with or without interactions between the intercalated lithium ions[2,3,7-9].

Recently, in order to investigate the ordering of the lithium ions in the $LiMn_2O_4$ electrode, Gao et al.[8] calculated the electrode potential vs. lithium composition curve with the lattice gas model using the Bragg-Williams approximation, and Kudo and Hibino [9] obtained theoretically the curve using the Bethe approximation. In spite of their satisfactory reproduction of the ordering of the lithium ions in the oxide, they did not actually apply those approximations to determination of the thermodynamic properties of the electrode. In order to understand the electrochemical lithium intercalation involving the ordering of the lithium ions more in details, quantitative determination of the thermodynamic properties of the electrode should be necessitated.

In this work the partial molar enthalpy and entropy for the lithium intercalation into the $Li_{1-\delta}Mn_2O_4$ electrode were theoretically calculated using the lattice gas model based upon the Bragg-Williams approximation and compared with experimental results. For this purpose, we employed galvanostatic intermittent titration technique (GITT) in combination with electromotive force (EMF)-temperature measurement.

EXPERIMENTAL

The carbon-dispersed composite electrode composed of the sol-gel derived $LiMn_2O_4$ powder, 6 wt.% Vulcan XC-72 carbon black and 2 wt.% PVDF (polyvinyliedene fluoride) was prepared as described previously[10]. A three-electrode electrochemical cell was employed for the electrochemical experiments. Both the reference and counter electrodes were lithium foil (Foote Mineral, U.S.A., purity 99.9%) and a 1 M solution of lithium perchlorate ($LiClO_4$) in propylene carbonate (PC) was used as the electrolyte.

GITT was employed to obtain the cell potential transient by using a Solartron 1287 electrochemical interface (ECI). Applying a constant current to the cell during 3600 s upon charging* at 25 °C, the resulting cell potential transients were recorded. The charge current was selected so that a change in lithium content of $\Delta\delta = 1$ for $Li_{1-\delta}Mn_2O_4$ would occur over 10 h. The deviation from the ideal stoichiometry of $LiMn_2O_4$, δ, was calculated from the mass of the oxide and the electrical charge that is transferred upon charging. After interruption of the current pulse, it required about 12 h to reach equilibrium to obtain uniform distribution of the lithium ions throughout the working electrode. Equilibrium was considered to have been reached when the

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*Upon charging the cell by application of anodic current, the lithium deintercalation occurs from the $Li_{1-\delta}Mn_2O_4$ electrode.

fluctuation of the open circuit potential fell below 0.1 mV_{Li/Li^+}. After that the open circuit potential was just recorded as an electrode potential at 25 °C.

In contrast to the change in the lithium content, upon altering temperature of the cell in the range of −15 to 30 °C, the shift of the electrode potential was so rapid that it took about 1 h to stabilize the electrode potential at constant temperature. The results of EMF measurement as a function of temperature were satisfactorily reproducible upon heating and cooling. All electrochemical experiments were conducted in a glove box (MECAPLEX GB94) filled with purified argon gas.

LATTICE GAS MODEL WITH BRAGG-WILLIAMS APPROXIMATION

To solve the ordering of the intercalated lithium ions in $LiMn_2O_4$, the lattice gas model based upon the Bragg-Williams approximation[2,8] was used in this work. The lithium ions in 8(a) sites in the cubic-spinel $LiMn_2O_4$ form a diamond lattice, which can be considered as two interpenetrating face-centred cubic sub-lattices separated by 1/4, 1/4, 1/4 as shown in Fig. 1. The interaction between the lithium ions was modelled by considering that each lithium ion has four nearest neighbours in the other sub-lattice and twelve second-nearest neighbours within the same sub-lattice. Therefore, the Gibbs free energy of the lattice composed of two sub-lattices can be written as[8]

$$G/N = U\sum_i (1-\delta)_i + 4J_1(1-\delta)_1(1-\delta)_2 + 6J_2\sum_i (1-\delta)_i^2 - T\sum_i S_i/N \qquad (1)$$

with $S_i = k\ln\{N!/[(1-\delta)_i N]!(\delta_i N)!\} \cong -k[(1-\delta)_i \ln(1-\delta)_i + \delta_i \ln\delta_i]$, i=1, 2 (2),

where U is the site energy for a lithium ion in 8(a) site; $(1-\delta)_i$, the lithium content in the sub-lattice i = 1, 2; J_1 and J_2, the two-body interactions due to the nearest neighbours and the second-nearest neighbours, respectively; N, the total number of sites in each sub-lattice; T, the absolute temperature; k, the Boltzmann constant, and S_i represents the configurational entropy of the sub-lattice i simplified by using the Stirling's approximation, $\ln N! = MnN - N$.

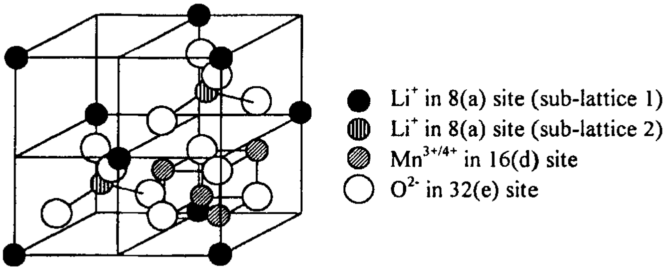

FIGURE 1 Schematic illustration of a cubic-spinel $LiMn_2O_4$ structure with a space group Fd3m.

Since the chemical potential of the lithium ion in total lattice, μ_{Li}, is equal to that chemical potential in the sub-lattice i, $\mu_{Li,i}$, i.e. $\mu_{Li} = \partial(G/N)/\partial(1-\delta)_1 = \partial(G/N)/\partial(1-\delta)_2$ at equilibrium, it can be derived from Eq. (1) and (2) that

$$\begin{aligned}\mu_{Li} &= \mu_{Li,1} = [U + 4J_1(1-\delta)_2 + 12J_2(1-\delta)_1] - T\{k\ln[\delta_1/(1-\delta)_1]\}\\ &= \mu_{Li,2} = [U+4J_1(1-\delta)_1 + 12J_2(1-\delta)_2] - T\{k\ln[\delta_2/(1-\delta)_2]\} \qquad (3).\end{aligned}$$

Considering that $\mu_{Li,1} - \mu_{Li,2} = 0$ from Eq. (3), we can calculate the values of $(1-\delta)_1$ and $(1-\delta)_2$ iteratively by a bisection method[11]. Therefore, the electrode potential E and the total lithium content $(1-\delta)$ in $Li_{1-\delta}Mn_2O_4$ can be obtained from $E = -\mu_{Li}/e$ and $(1-\delta) = [(1-\delta)_1+(1-\delta)_2]/2$, respectively.

RESULTS AND DISCUSSION

Figure 2 gives the electrode potential vs. lithium content curve and the plots of $(1-\delta)_1$ and $(1-\delta)_2$ with respect to $(1-\delta)$, calculated theoretically for the case of $U = -4.12$ eV, $J_1 = 37.5$ meV, $J_2 = -4.0$ meV and $T = 298$ K[8]. The calculated electrode potential curve showed a steep potential drop at $(1-\delta) = 0.5$, due to the ordering of the intercalated lithium ions[1,2,8,9]. The order-disorder phase transition occurs at the boundaries where the peaks appear in the derivative $-d(1-\delta)/dE$ vs. E[1,2,8].

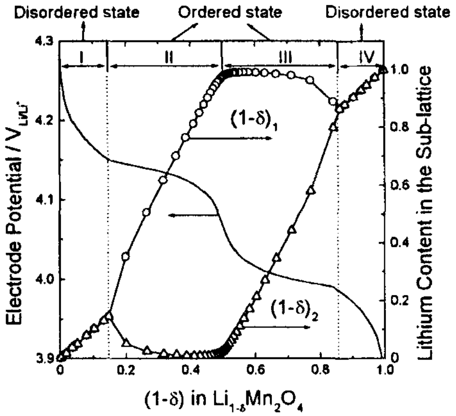

FIGURE 2 Electrode potential vs. lithium content curve and plots of $(1-\delta)_1$ (O) and $(1-\delta)_2$ (Δ) with respect to $(1-\delta)$ calculated theoretically for the case of $U = -4.12$ eV, $J_1 = 37.5$ meV, $J_2 = -4.0$ meV and $T = 298$ K. The vertical dashed lines, representing the boundaries between the ordered and disordered phases, were determined at the points where the sharp peaks appear in $-d(1-\delta)/dE$ vs. E curve.

In Fig. 2, $(1-\delta)_1$ and $(1-\delta)_2$ are equal in value with $(1-\delta)$ at the same electrode potential in the range of $0 < (1-\delta) < 0.15$ and $0.85 < (1-\delta) < 1$ as denoted as region I and IV, respectively. This means that the intercalated lithium ions in the 8(a) sites are distributed randomly within the whole lattice. In contrast, $(1-\delta)_1$ and $(1-\delta)_2$ deviate severely from $(1-\delta)$ in the range of $0.15 < (1-\delta) < 0.85$, indicating that the ordering of the lithium ions takes place. As the lithium intercalation proceeds into the $Li_{1-\delta}Mn_2O_4$ electrode within the ordered state designated as region II, the lithium ions mainly reside at 8(a) sites in the sub-lattice 1. In the region III, the lithium ions are newly intercalated into the sites in the sub-lattice 2, whereas the sites in the sub-lattice 1 are completely occupied by the previously intercalated lithium ions.

Figure 3 presents the temperature dependence of the electrode potential which is theoretically calculated from Eq. (3) and simultaneously experimentally obtained from the cell of Li/$LiClO_4$-PC solution/$Li_{1-\delta}Mn_2O_4$ electrode at various lithium contents $(1-\delta)$ in the temperature range from 258 to 303 K. Both the curves share nearly the same values. For clarity both curves are separated each other by 0.1 V. Both theoretical and experimental electrode potentials alike increased with temperature in the region I and III, but they markedly decreased in the region II and IV. In order to quantitatively analyse the complicated temperature dependence of the electrode potential, let us introduce the partial molar thermodynamic quantities for the lithium intercalation into the $Li_{1-\delta}Mn_2O_4$ electrode.

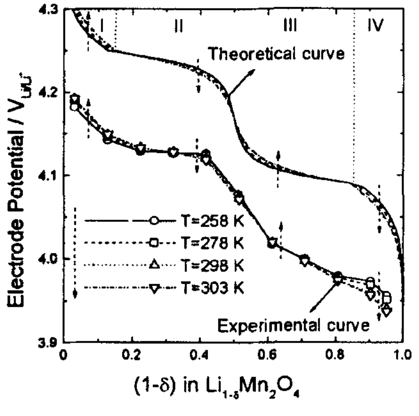

FIGURE 3 Temperature dependence of the electrode potential which is theoretically calculated from Eq. (3) and experimentally obtained from the cell of Li/$LiClO_4$-PC solution/$Li_{1-\delta}Mn_2O_4$ electrode at various lithium contents $(1-\delta)$ in the temperature range from 258 to 303 K. The theoretical electrode potential curves are shifted up to 0.1 V for clarity.

In Eq. (3), the first and second terms multiplied by the Faraday constant F are just equal to the partial molar intercalation enthalpy and entropy of the lithium ion in the sub-lattice i, respectively, i.e. $\Delta\bar{H}_{Li,i}=F[\partial(H/N)/\partial(1-\delta)_i]$ and $\Delta\bar{S}_{Li,i}=F[\partial(S/N)/\partial(1-\delta)_i]$. Therefore, the theoretical partial molar enthalpy and entropy for the lithium intercalation into total lattice are given by

$$\Delta\bar{H}_{Li} = F[\partial(H/N)/\partial(1-\delta)] = \sum_i \Delta\bar{H}_{Li,i}[d(1-\delta)_i/d(1-\delta)]/2 \quad (4),$$

$$\Delta\bar{S}_{Li} = F[\partial(S/N)/\partial(1-\delta)] = \sum_i \Delta\bar{S}_{Li,i}[d(1-\delta)_i/d(1-\delta)]/2, \quad i = 1, 2 \quad (5).$$

Since $(1-\delta)_1$ and $(1-\delta)_2$ are not independent variables, the derivatives $[d(1-\delta)_1/d(1-\delta)]$ and $[d(1-\delta)_2/d(1-\delta)]$ can be calculated numerically from the plots of $(1-\delta)_1$ and $(1-\delta)_2$ vs. $(1-\delta)$ in Fig. 2.

The experimental partial molar enthalpy and entropy were determined from the variation of the partial molar Gibbs free energy with temperature by the same way as previously reported[4-6]. Figure 4 illustrates the temperature dependence of the partial molar intercalation Gibbs free energy obtained from the experimental results in Fig. 3 by using $\Delta\bar{G}_{Li} = -FE$. Since $\Delta\bar{G}_{Li}$ showed a linear variation with temperature, $\Delta\bar{H}_{Li}$ and $\Delta\bar{S}_{Li}$ can be considered to be independent of temperature and then simply determined by using $\Delta\bar{H}_{Li} = -F[E-T(\partial E/\partial T)]$ and $\Delta\bar{S}_{Li} = F(\partial E/\partial T)$.

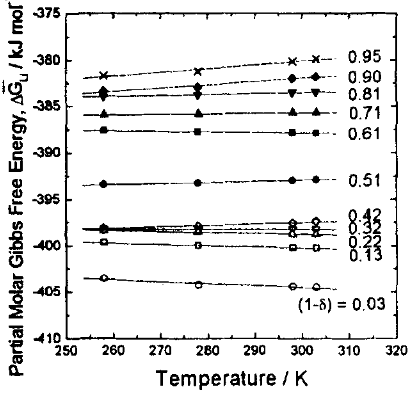

FIGURE 4 Variation of the partial molar intercalation Gibbs free energy of the lithium ion with temperature obtained from the experimental results in Fig. 3 by using $\Delta\bar{G}_{Li} = -FE$ at various lithium contents $(1-\delta)$ as indicated in the figure.

Figures 5(a) and 5(b) demonstrate the plots of the partial molar enthalpy and entropy vs. lithium content $(1-\delta)$, respectively, determined theoretically and experimentally at 298 K. The experimental partial molar quantities were well consistent with the theoretically calculated values. If the lithium intercalation proceeds into the disordered state of total lattice in the whole range of $(1-\delta)$, the enthalpy increases linearly and the entropy decreases monotonically with $(1-\delta)$ as indicated as the dashed lines in Figs. 5(a) and 5(b), respectively. It has been reported[4-6] that the linear increase of the enthalpy is mainly attributable to the increase in the repulsive interaction energy between the lithium ions. The monotonic decrease of the entropy can be ascribed to the decrease in the number of the vacant 8(a) sites. By contrast, the theoretical partial molar enthalpy and entropy deviate severely from the ideal behaviour in the region II and III, bearing in mind that Fig. 2 showed the strong difference between both lithium contents in two sub-lattices caused by the ordering of the lithium ions.

In the region II, since $(1-\delta)_1$ increases abruptly with $(1-\delta)$ whereas $(1-\delta)_2$ remains nearly zero as discussed above in Fig. 2, $d(1-\delta)_1/d(1-\delta)$ is larger in value than $d(1-\delta)_2/d(1-\delta)$ which is almost zero, suggesting from Eq. (4) that $\Delta\bar{H}_{Li,1}$ contributes dominantly to $\Delta\bar{H}_{Li}$. Therefore, a negative deviation of $\Delta\bar{H}_{Li}$ from the ideal behaviour is owing to the attractive interaction energy between the lithium ions in the same sub-lattice 1. In contrast, in the region III where $(1-\delta)_2$ increases abruptly with $(1-\delta)$ and $(1-\delta)_1$ is nearly unity, $d(1-\delta)_2/d(1-\delta)$ is larger in value than $d(1-\delta)_1/d(1-\delta)$ which is nearly zero. This means that $\Delta\bar{H}_{Li}$ is primarily affected by $\Delta\bar{H}_{Li,2}$ which shows a positive deviation from the ideal behaviour because of the strong repulsive interaction energy between the lithium ions in the sub-lattice 1 and 2.

Similarly, it is suggested from Eq. (5) that the partial molar entropy for the lithium intercalation into the lattice is significantly affected by the change of $(1-\delta)_1$ in the region II and that of $(1-d)_2$ in the region III. In the region II, $(1-\delta)_1$ is larger in value than $(1-\delta)$, due to the ordering of the lithium ions. As a result, $\Delta\bar{S}_{Li}$, which is dominantly controlled by $\Delta\bar{S}_{Li,1}$, shows a negative deviation in the region II. A positive deviation in the region III is mainly because $(1-\delta)_2$ is smaller in value with respect to $(1-\delta)$.

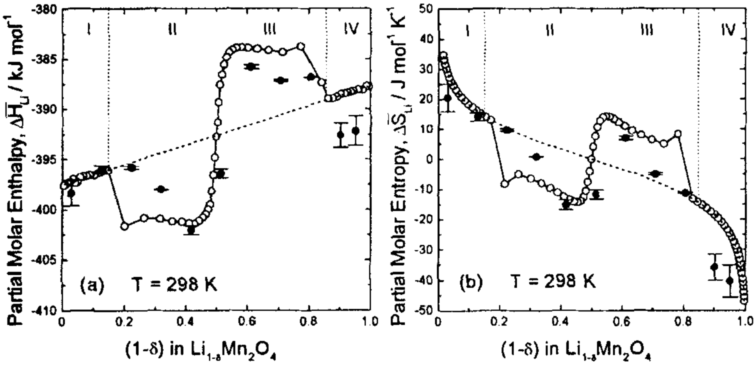

FIGURE 5 Plots of the partial molar (a) enthalpy and (b) entropy vs. lithium content $(1-\delta)$ calculated theoretically (–O– by the solid line) and determined experimentally (●) at 298 K. The dashed lines represent the partial molar enthalpy and entropy calculated under the assumption that the lithium intercalation proceeds into the disordered state of total lattice in the whole range of $(1-\delta)$.

CONCLUSIONS

1. From the numerical calculation using the lattice gas model with the Bragg-Williams approximation, it was found that both lithium contents in two sub-

lattices deviate strongly from that lithium content in total lattice due to the ordering of the intercalated lithium ions in the $Li_{1-\delta}Mn_2O_4$ electrode.

2. The theoretical partial molar intercalation enthalpy and entropy of the lithium ion calculated by a numerical method are in a good agreement with experimental results obtained from the temperature dependence of the electrode potential at various lithium contents. The complicated variation of the electrode potential curves with temperature was quantitatively analysed on the basis of the ordering of the lithium ions from the thermodynamic view point.

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